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Ultrasonic attenuation properties of glassy alloys in views of complex viscoelasticity

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Using ultrasonics, acoustic attenuation characteristics of $Pd_{40}Cu_{30}P_{20}Ni_{10}$, $Zr_{65}Pd_{12.5}Ni_{10}Al_{7.5}Cu_5$, $Cu_{55}Zr_{30}Ti_{10}Pd_5$, and $Ti_{41.5}Cu_{47.5}Ni_{7.5}Hf_5Zr_{2.5}Sn_1$ glassy alloys were examined in comparison with crystalline metals based on complex viscoelasticity. The glassy alloys favor to absorb the longitudinal one, but crystalline materials absorb the shear one, associated with periodicity and randomness of energy potentials, respectively. In sharp contrast to crystalline materials, Nyquist [Bell Syst. Tech. J. **11**, 126 (1932)] diagrams of the glassy alloys are characterized by large areas of the third and the fourth quadrant in the loop, suggesting advancement of the relay in phase, that is, increment of the imaginary parts in complex waves. *© 2007 American Institute of Physics.*
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The glassy alloys are the last frontier of metals and metallic alloys. Since 1960, when Klement *et al.*[1] discovered amorphous alloys in the Au–Si system, a number of works have been carried out for preparation and properties of various amorphous and glassy alloys.[2–5] Especially glassy alloys have characteristic physical and chemical properties such as high strength, high corrosion resistance, and good soft magnetic properties, which are significantly different from the corresponding crystalline alloys. Special interest focuses on glass-forming ability associated with formation of metastable polyhedra,[6] and mechanism of glass transition by a free volume related kinetic phenomenon.[7] However, in addition to these characteristics, it is also important to examine their acoustic attenuation properties. In propagation of an acoustic wave which is mainly phonon velocity, acoustic energy generally decreases by absorption and scattering. The acoustic scattering effect plays an important part in evaluation for structural morphology and viscoelasticity of glassy phase.

Our interests lie in determining dilational and shear attenuation coefficients and dynamic viscosity of representative glassy alloys, $Pd_{40}Cu_{30}P_{20}Ni_{10}$ (composition is given in nominal at. %),[8] $Zr_{65}Pd_{12.5}Ni_{10}Al_{7.5}Cu_5$,[9] $Cu_{55}Zr_{30}Ti_{10}Pd_5$,[10] and $Ti_{41.5}Cu_{47.5}Ni_{7.5}Hf_5Zr_{2.5}Sn_1$, in views of complex viscoelasticity. The Pd-based and other alloys represent metal/metalloid and metal/metal bonding-type cluster structures, respectively. The metal/metalloid bonding has some covalency and the metal/metal one mainly shows metallic bonding. Therefore, there is a possibility that the acoustic scattering effect is different in these two types of glassy alloys. Strictly speaking, the bonding nature of the latter would be also different from one another. However, no research work has been carried out previously on measurement of these attenuation parameters for the glassy alloys using both longitudinal and shear waves with the same frequency. Since the dilational attenuation is sensitive to variation of energy potentials between atoms and the shear one is sensitive to atomic rearrangements in solids and fluid viscosity,[11] the measurement by both waves provides much useful information about inelastic and damping contributions for glassy alloys.

The ingots of alloys studied were prepared by arc-melting mixtures of Pd, Cu, Ni, Zr, Hf, Al, Ti, Ag, and Sn metals with 99.8 mass % purity in a Ti-gettered argon atmosphere. Melting was repeated four times to ensure chemical homogeneity. From these ingots, bulk glassy rod-shaped samples 3–5 mm in diameter and 45 mm in length were prepared by the copper mold casting technique. The bulk samples were used for measurement of density and damping properties. The density was measured by Archimedes's prin-

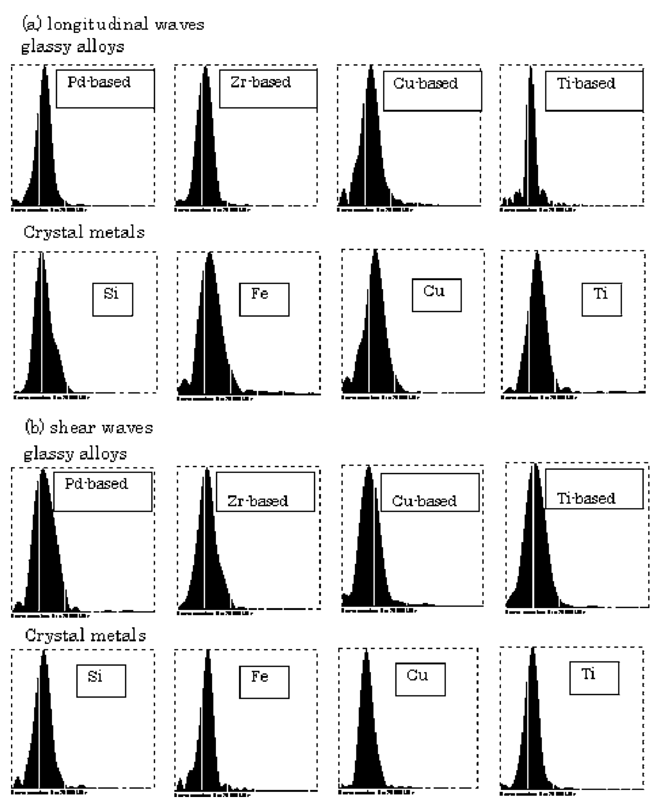

FIG. 1. Power spectra of receiving waves for longitudinal (a) and shear (b) waves of four kinds of glassy alloys and four kinds of crystalline metals.

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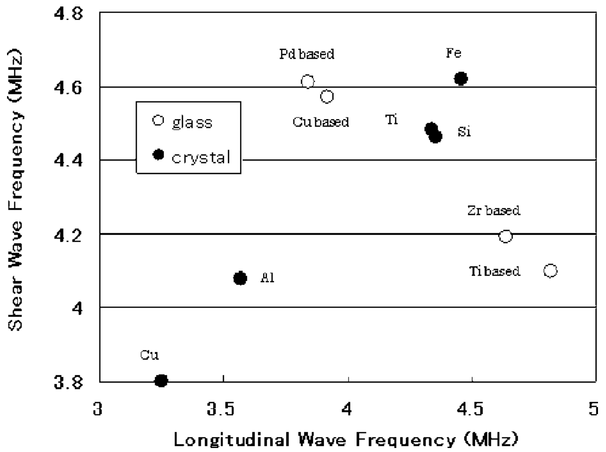

FIG. 2. Main frequencies of receiving longitudinal shear waves for glassy alloys and crystalline metals.

ciple by weighing ingots in tetrabromoethane and in air. The structure of the sample was analyzed with an x-ray diffractometer using Cu $K\alpha$ source. All the samples were in a glassy phase state.

Dilational and shear wave attenuation coefficients, and dilational and bulk dynamic viscosities were measured by use of an ultrasonic diagnosis and analyzer (TP-1001, Toshiba Tungaloy) at 298 K using longitudinal and shear waves with a frequency of 5 MHz. The transducers were contacted at both edges of the specimen under a pressure of 0.2 MPa by water-free naphthenic hydrocarbon couplant oil[12] (Tungsonic Oil H). The experimental procedure has been described in our previous papers.[13]

As bulk glassy alloys are generally multicomponent[14] (usually quaternary or at least ternary, and just a few binary glassy alloys 1–2 mm in critical size are known) on heating they either undergo a multistage crystallization process or form several crystalline phases simultaneously by eutectic reaction.[15] However, even if a single-type crystalline or quasicrystalline icosahedral phase (metastable, as a rule) is formed at the primary crystallization stage (which takes place in Cu- and Zr- based alloys studied in the present work) it coexists with a residual glassy phase.[9] For justice, one should say that the formation of a single metastable crystalline phase is observed in some amorphous alloys by a polymorphous mechanism but such a behavior is generally found in the marginal glass formers which require a high cooling rate for vitrification and cannot be prepared in a bulk form.[15] A large sample size of at least 3 mm is required for ultrasonic measurements. Since it is impossible to evaluate their attenuation properties, we used pure metals of Fe, Cu, Ti, and Si as the comparative crystalline metals for the glassy alloys.

When waves with nominal frequencies above 2 MHz are propagated through the specimens, the waves with high frequencies are mostly absorbed. The power spectra of receiving longitudinal and shear waves of four kinds of glassy alloys and four kinds of representative crystalline metals are shown in Fig. 1. The power spectra of glassy alloys are broader, compared with crystalline metals, suggesting evidences of different absorption mechanisms for both materials. To compare the absorption behaviors for the glassy and crystalline materials, the main frequencies of longitudinal and shear receiving waves for both materials are plotted in Fig. 2. The glassy alloys favor to absorb the longitudinal one, but the crystal metals absorb the transverse one. Assuming from the sharply contrasting results, the cyclic energy potentials of crystals would facilitate the propagation of the longitudinal phonons, while the disturbance of the transverse phonons could be prevented from the randomness of the potentials in glassy alloys.

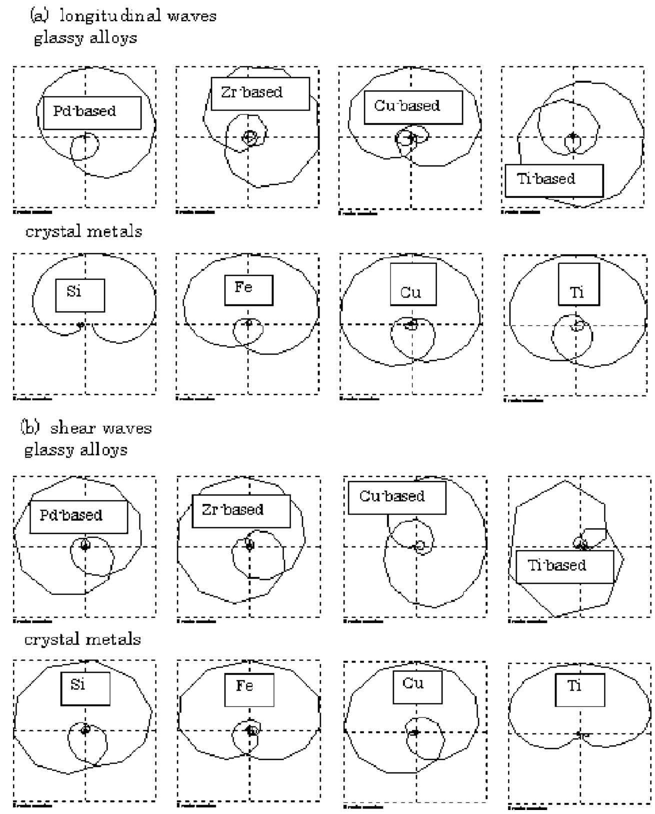

FIG. 3. Nyquist diagrams of receiving waves for longitudinal (a) and shear (b) waves of four kinds of glassy alloys and four kinds of crystalline metals.

To determine modulation of the propagated wave patterns for glassy alloys, we next pay attention to the Nyquist diagram for the propagated waves. The Nyquist diagram was plotted in the complex plane of the open-loop transfer (propagation) wave function for all the complex frequencies in counterclockwise, using a vector locus of phase ϕ.[16] Fourier transformation of the digitized receiving wave forms from the dispersive media is carried out to determine the main frequency f and ϕ at f.

TABLE I. Dilational and shear attenuation coefficients and their ratios for materials used in this study.

Materials	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	$Zr_{65}Ni_{10}Cu_5Al_{7.5}Pd_{12.5}$	$Cu_{45}Zr_{45}Ag_{10}$	$Ti_{41.5}Cu_{47.5}Hf_5Zr_{2.5}Ni_{7.5}Sn_1$	Fe	Cu	Ti	Si	Al
α_l	0.13	1.56	1.00	0.38	0.39	0.38	0.36	0.97	0.25
α_s	0.07	0.70	0.59	0.35	0.17	0.37	0.85	0.29	0.20
α_l/α_s	0.55	0.45	0.59	0.93	0.42	0.98	0.85	0.30	0.81

$$\mathrm{Im}(\omega)/Re(\omega) = \tan\phi. \tag{1}$$

The Nyquist diagrams for four kinds of glassy alloys and four kinds of crystalline metals are shown in Fig. 3. The diagrams for crystalline metals are characterized by small areas of the third and the fourth quadrant in the loop, while the diagrams for the glassy alloys tend to have relatively large areas of the third and the fourth quadrant. The tendency of the latter is remarkable for the transverse one. The large area of the third and the fourth quadrant suggests advancement of delay in phase, that is, increment of the imaginary parts in the complex waves.[17] The delay in phase modulation of the complex waves was observed in thermal degradation for rubbers[18] and polyvinyl chloride (PVC),[19] accompanied by regression in viscoelasticity, described later. The former is characterized by the formation of dangling ends in degraded rubbers, while the latter is associated with occurrence of chain scission in degraded PVC. The common point of both degraded materials is disorder in the mesoscopic structure. Hence, by analogy it is clear that the glassy alloys have a mesoscopic disorder for propagation of acoustic waves. The disorder corresponds to randomness of the energy potentials.

Table I shows the longitudinal and transverse attenuation coefficients α_l and α_s, respectively, for four kinds of glassy alloys and five kinds of crystalline metals, along with a ratio of coefficients, α_l/α_s. The α_l and α_s of Zr- and Cu-based glassy alloys are higher than those of other materials, while the α_l and α_s of the Pd-based glassy alloy shows the lowest values (0.13 and 0.07 Np/cm, respectively) among all kinds of materials of interests. Since the Pd-based alloy is a metal/metalloid bonding-type alloy and other alloys have the metal/metal-type bonding, the opposite attenuation behavior could be explained by the bonding type of clusters in the glassy alloys. Especially, the highest propagation ability for acoustic waves in the Pd-based alloy would be responsible for the tight atomic bonding of a trigonal prism capped with three half octahedra and a tetragonal dodecahedron found in $Pd_{1.5}Cu_{2.5}P$, because their higher coordination numbers for metallic atoms are over 12.[20] On the other hand, the ratios of α_l/α_s for Ti-based alloy and crystalline Cu, Al, and Ti metals are higher than those obtained for other metals used in this study. This may be associated with the slipping nature in metal/metal bonding,[21] as well as Cu and Al metals having fcc structure with small stacking fault energy.

The eventual thermodynamic behavior of glassy alloys such as macromolecules must involve a Newtonian viscous component to the elastic response; such a situation is denoted as viscoelasticity, associated with complex waves.[13] In order to investigate the viscoelastic effect, we calculate the dynamic viscosity η of the glassy alloys.

Equation (1) can be synonymously expressed by a complex elasticity M^*,[22]

$$M^* = M_1 + i\omega\eta, \tag{2}$$

where M_1 is a dynamic elasticity. Since glassy alloys are three-dimensionally elastically homogeneous bodies, we can use the following formulas for dilational, shear, and volumetric dynamic viscosities, η_l, η_s, and η_v, respectively,

$$\eta_v = \eta_K + 4/3\,\eta_s, \tag{3}$$

$$\eta_K = K/\omega, \tag{4}$$

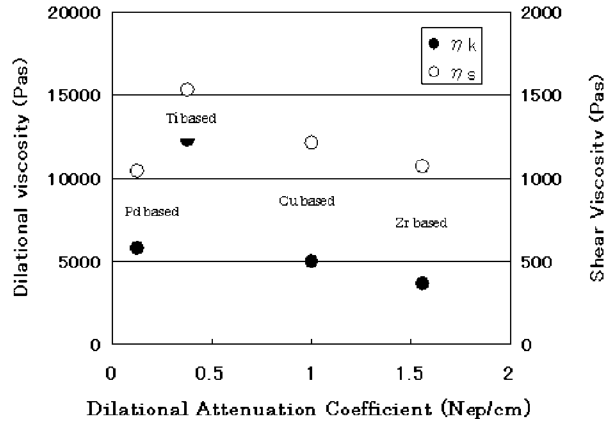

FIG. 4. Relation between shear and bulk dynamic viscosityies and dilational attenuation coefficient for glassy alloys.

$$\eta_\sigma = G/\omega, \tag{5}$$

where $\omega=2\pi f$. The attenuation coefficient dependency on shear and volumetric dynamic viscosities is presented in Fig. 4. In metal/metal bonding-type alloys, both dynamic viscosities decrease with increasing the attenuation coefficients. From the complex wave elasticity, furthermore, the viscoelasticity of the glassy alloys is predominated by volumetric motion. Judging from the above mentioned results, these inelastic parameters are sensitive probes for evaluating the acoustic damping and viscoelasticity of glassy alloys, associated with the complex elasticity.

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